

# PATENT SPECIFICATION

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(19)



## (54) DRYING PROCESS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention relates to a process for removing water from the off-gas streams from phosgenation processes carried out in inert solvents.
- 15 In phosgenation reactions, i.e. reactions which involve the use of phosgene as a reaction component, for example processes for the manufacture of isocyanates or chloroformates from primary amines or hydroxy compounds respectively, hydrogen chloride is evolved as a by product.
- 20 The hydrogen chloride is evolved in the gaseous state generally in admixture with excess phosgene and with inert solvent vapour, if, as is normally the case, the reaction is being carried out in the presence of an inert solvent. In order to operate economically it is necessary to recover the phosgene, hydrogen chloride and the solvent and in many processes the phosgene and solvent are recovered and recycled direct into the phosgenation process if this is carried out in a continuous manner.
- 25 Isocyanates and chloroformates are extremely reactive towards water and if water is present during their preparation this leads to the formation of by-products and to loss of yield of the desired isocyanate or chloroformate. Although precautions are always taken to exclude water it has proved impossible to exclude water completely as small amounts are introduced via the starting materials and solvents which may contain as much as 0.05% by weight, there is also the possibility of a small ingress of water from leaks. It is essential that if possible this water should be eliminated, particularly in continuous processes where if not removed it would recirculate with the solvent until it finally reacted with isocyanate
- [Price 33p]

with consequent loss of yield in the case of isocyanates which are to be isolated by distillation. Where isocyanates are not distilled the reaction with water results in the formation of ureas which can profoundly alter the characteristics and properties of the product.

In addition, the presence of even small amounts of water can set up serious corrosion in the plant on account of the large amount of hydrogen chloride present during the actual phosgenation reaction. Not only does corrosion cause serious damage to the plant but it impairs the quality of the product particularly if it is to be solid as an undistilled product. This reduces the value of the product because of the catalytic effect on polyurethane reactions of iron and other transition metals which can be introduced into the product by the corrosion of mild or stainless steel plant. In consequence it is desirable to control the iron content of undistilled isocyanate products to a low and consistent level.

The present invention is directed at the elimination of water from the reactor and work-up system to prevent degradation of isocyanate groups, to limiting corrosion and to controlling the amount of iron and transition metals in undistilled isocyanate products to a low level.

Essential features of phosgenation processes are (a) that reaction is carried out in the presence of a solvent, frequently a chlorinated hydrocarbon being used (b) that the solvent is recovered and reused, and (c) that an excess of phosgene is employed. If the solvent becomes contaminated with a small amount of water, then when it is recovered the water is not removed and the solvent when returned to the process can cause corrosion. Although phosgene is present in excess, its reaction with water in low concentration, particularly if hydrogen chloride is present in very low. It is well-known that the reaction of phosgene with water to give carbon dioxide and hydrogen chloride is catalysed by a variety of agents, for example carbon and alumina. Proposals have been made to dry the off-gases from a phosgenation system by drying the hydrogen

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chloride and phosgene vapour after condensation of the solvent used in the reaction but although this procedure results in a purer and less-corrosive off-gas stream it does nothing to inhibit corrosion in the main phosgenation plant or to prevent contamination of the product with corrosion products containing metal compounds.

The reaction of both isocyanates and phosgene with low concentrations of water may be very slow unless catalysed but corrosion by aqueous hydrogen chloride in a phosgenation system may be serious even at extremely low levels of water content.

We have found that drying agents and catalytic hydrolysis agents are not particularly effective under the conditions described in the prior art. Although the water content is reduced to a small extent it is not decreased by a sufficient amount to have a significant effect on the rate of corrosion and the build-up of iron and other metals in the product.

We have now discovered that the agents already described have a very much greater activity provided they are not wetted by solvent and provided that the solvent is maintained in the vapour phase preferably above 100°C.

Thus according to the present invention there is provided a process for eliminating or reducing water in a phosgenation reaction system which comprises passing the off-gases therefrom at a temperature above the condensation point of phosgenation solvent, the pressure used, through a bed of a catalytic agent which accelerates the reaction of water with phosgene, and then cooling the vapour stream to condense dried solvent which is re-used in the process.

Small amounts of water introduced with the raw materials and from steam and water leaks are thus continually removed from the system, a solvent stream of very low moisture content is returned for re-use and off-gases comprising HCl and phosgene also of low water content are produced.

The process is particularly applicable to phosgenation reaction systems used for the preparation of organic isocyanates.

By the term catalytic agent is intended an agent normally known to catalyse the hydrolysis of phosgene.

Examples of catalytic agents which may be used include silica gel, alumina, activated carbon, anhydrous calcium sulphate (sold commercially under the trade name Drierite) and Zeosorb (a Registered Trade Mark).

A large number of such drying agents operate both as normal drying agents and as catalytic hydrolysis agents for the destruction of phosgene, that is, in addition to a normal drying action by absorption of moisture they also catalyse the reaction between phosgene and water removing the water present by reac-

tion with a small amount of the excess phosgene.

Particularly effective agents are anhydrous calcium sulphate, activated carbon and alumina.

The drying operation may be carried out at any convenient point in an off-gas stream from a phosgenation reaction system or from a subsequent work-up stage. Phosgenation is usually carried out in dilute solution and the solvent used together with the excess of phosgene employed is normally recovered by evaporation of the isocyanate solution in one or more column evaporators. These may be packed columns, climbing film evaporators or proprietary thin-film evaporators. Hydrogen chloride produced during the reaction is eliminated simultaneously with the solvent and excess phosgene. The drying process may be carried out by passing the vapour stream from any of the evaporators through a vessel packed with the chosen catalytic agent providing that the temperature in the drying vessel is maintained at a sufficiently high temperature to prevent any condensation of solvent. A vapour stream comprising excess phosgene, hydrogen chloride and some solvent is also evolved from the phosgenation reactors themselves and the drying process may be carried out at this stage if desired by passing the vapour stream through a vessel packed with the catalytic agent and provided with sufficient heating to prevent condensation of solvent.

Whichever point of the process is used for the drying stage the vapour, after passing through its catalyst bed, passes to a condenser or condensers from which solvent of low moisture content is removed.

Any of the techniques used in the normal drying of a gas may be used in the present process. Thus the vapour stream may be passed over layers of the catalytic agent spread on trays or through a column packed with the agent with or without a support. It is of the utmost importance that the agent is not wetted by solvent or condensate when it is in operation; if this happens drying efficiency becomes very low. In order to use the drying process on a commercial scale, it is desirable that a compact catalyst packed vessel of relatively low cost be employed.

It is an essential feature of the process that any solvent passing through the drying zone be in the vapour state. Thus the drying must be carried out at such a temperature that the solvent is maintained in the vapour phase. It is not necessarily essential to maintain the drying zone at a temperature above the boiling point of the solvent as a mixture of phosgene or hydrogen chloride with solvent can be completely in the vapour phase at temperatures below the boiling point of the solvent. It is only essential to maintain such a temperature that the solvent is in the

vapour state. This temperature varies with the nature of the solvent and the composition of the vapour stream.

Although the temperature may be above that required to maintain the solvent in the vapour state, the efficiency of the particular drying agent employed must be borne in mind, for example Drierite is much less effective at temperature of 160° than at 120°C and a preferred temperature with Drierite is 100—160°C.

Solvents used in phosgenation reactions do not contain active-hydrogen atoms, that is hydrogen atoms which take part in the Zerevitinoff reaction. Solvents commonly used include esters, hydrocarbons and in particular chlorinated hydrocarbons such as monochlorobenzene, ortho - dichlorobenzene, methylene dichloride and carbon tetrachloride.

Removal of the water considerably reduces corrosion in phosgenation plants in particular those operating continuously with recycling of solvent and excess phosgene. It also minimises production of by-products by the water/iso-

cyanate reaction, thus improving the isocyanate yield. 25

The invention is illustrated by the following examples:—

#### Example 1

A vapour stream of the same constitution as that issuing from the top of a recovery column in which monochlorobenzene was condensed on recovery from a phosgenation plant, was prepared on the laboratory scale and had the following composition by volume: 30

50 ml/minute phosgene  
100 ml/minute monochlorobenzene vapour  
50 ml/minute N<sub>2</sub> containing 20,000 p.p.m. V/V of water vapour. 35

This stream was passed in the vapour phase at 110°C through a drying tower packed with a drying agent as listed below and the water content of the issuing gas measured after passage of the stream for 2 hours and 64 hours. The results together with those for an experiment in which no drying agent was present are tabulated below. 40 45

TABLE I

50	Column Packing	Particle Size	Flow rate m <sup>3</sup> /pm/m <sup>3</sup> packing	Measured water content of outlet gas stream p.p.m. V/V	
				After 2 hours	After 64 hours
55	None	—	932	>>3000	>>3000
	Activated carbon	8—12 mesh	932	100	100
	Drierite	6—8 mesh	932	100	40

The relationship between mesh number and aperture size i.e. particle size is given in British Standard 410: 1969.

During one short period of the 64 hour run using Drierite the conditions of temperature in the column were so adjusted that monochlorobenzene was allowed to condense on the packing in the drying tower and it was found that the water content of the issuing gas then rose rapidly to >3000 p.p.m. On restoring the original conditions so that the condensed solvent was evaporated the water content of the issuing gas stream fell rapidly to the low level given in the table.

A comparative experiment was also carried out in which a condenser was fixed above the drying tower and a portion of the issuing monochlorobenzene was condensed and allowed to flow back in the liquid state on to the drying tower packing. All the other conditions were the same as those given above and it was found that under these conditions the water content of the issuing gas never fell below

3000 p.p.m. V/V with either Drierite or activated carbon packing. 80

The above example illustrates the efficiency of removing water with the solvent in the vapour phase and the complete failure when the solvent is in the liquid phase. 85

#### Example 2

An experiment similar to that of Example 1 was carried out using the same conditions, temperature and gas feed. After leaving the packed column, the vapour stream was condensed. Test pieces of mild steel and stainless steel were immersed in the condensate contained in a small catch-pot from which it flowed continuously to storage. The temperature of the condensate was approximately 100°C. 90 95

The column was packed with Drierite but controls were also run with the packing omitted.

The following results illustrate the effect on corrosion of removing water from the system. 100

Test piece	Column packing	Rate of corrosion
Mild steel	Drierite	negligible
Mild steel	None	10 mm/year
Stainless steel		
(type 18/10 Mo-Ti)	Drierite	negligible
Stainless steel		
(type 18/10 Mo-Ti)	None	2 mm/year

### Example 3

10 An experiment similar to that of Example 1 was carried out using ortho-dichlorobenzene in place of monochlorobenzene, the drying agent used was Drierite. The flow of phosgene, nitrogen and water vapour was the same as in Example 1 and the flow of solvent was

15 adjusted so as to obtain a maximum concentration of solvent vapour without any condensation on the catalyst bed. The temperature of the drying tower was varied, with the results given below.

	Drier Temperature °C	Water content of outlet gas p.p.m. V/V
20	117	24
	140	35
25	150	160
	160	600
	170	3000

30 Thus it is shown that the efficiency of Drierite decreases with increasing temperature and becomes negligible at 170°C. As would be expected it is clear that the temperature of the vapour stream should be adjusted to within the range where the particular drying agent is efficient.

35 A similar experiment carried out using activated carbon as the drying agent showed that at 170°C an activated carbon packed drying column reduced the water content of the issuing gas stream to 40 p.p.m. V/V.

### WHAT WE CLAIM IS:—

1. A process for eliminating or reducing water in a phosgenation reaction system which comprises passing the off-gases therefrom at a temperature above the condensation point of the phosgenation solvent at the pressure used, through a bed of a catalytic agent as hereinbefore defined which accelerates the reaction of water with phosgene, and then cooling the vapour stream to condense dried solvent which is re-used in the process.

2. A process as claimed in Claim 1 wherein the phosgenation reaction system is one used for the preparation of organic isocyanates.

3. A process as claimed in Claim 1 or Claim 2 wherein the catalytic agent is anhydrous calcium sulphate, activated carbon or alumina.

4. A process as claimed in Claim 3 wherein the catalytic agent is anhydrous calcium sulphate at a temperature of from 100—160°C.

5. A process as claimed in any one of the preceding claims wherein the solvent employed in the phosgenation process is a chlorinated hydrocarbon.

6. A process according to Claim 1 as hereinbefore described especially with reference to the examples.

7. A phosgenation process wherein elimination or reduction of water is carried out by a process as claimed in the preceding claims.

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